

AMENDMENTS TO THE CLAIMS

The following is a complete listing of the claims that replaces all previous versions.

1.-85. (Canceled)

86. (Previously presented) A process for atom transfer radical addition for adding functionality to an oligomer or polymer, comprising:

reacting a first oligomer or polymer having a radically transferable atom or group with a second compound having a first desired functional group, the second compound reactive with the first oligomer or polymer after removal of the radically transferable atom or group, wherein the second compound is not a free radically polymerizable monomer, in the presence of a system comprising:

a catalyst which participates in a reversible cycle with the first oligomer or polymer.

87. (Original) The process of claim 86, wherein the catalyst comprises a transition metal salt.

88. (Original) The process of claim 86, wherein the catalyst comprises a transition metal and further comprising:

adding the transition metal in its metal zero state.

89. (Canceled)

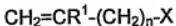
90. (Previously presented) The process of claim 86, wherein the second compound comprises a α,α -disubstituted olefin group.

91. (Original) The process of claim 86, wherein the catalyst is a transition metal complex.

92. (Previously Presented) The process of claim 91, wherein the transition metal complex comprises a transition metal and a ligand, and the process further comprises adding additional transition metal and, optionally, additional ligand.

93. (Original) The process of claim 86, further comprising forming a second oligomer or polymer which is not polymerizable in the system.

94. (Original) The process of claim 93, further comprising reacting the second oligomer or polymer with a second compound which is reactive with the second oligomer or polymer, wherein the second compound has a second desired functional group.
95. (Original) The process of claim 94, wherein the second compound additionally comprises a fourth desired functional group, the functional groups are thereby incorporated into the polymer at each reactive chain end, wherein the third compound has a structure:



wherein R¹ is selected from H, CH₃ or aryl;

n is an integer; and,

X is a functional group.

96. (Original) The process of claim 86, wherein the first oligomer or polymer has a plurality of radically transferable atoms or groups.
97. (Original) The process of claim 93, wherein the second polymer is one of a homotelechelic-polymer or a heterotelechelic polymer.
98. (Original) The process of claim 97, wherein the second desired functional group is subject to further reaction conditions to convert the second functional group into a third functional group.
99. (Previously Presented) The process of claim 98, wherein the said third functional group comprises a double bond.
100. (Previously Presented) The process of claim 99, wherein the said further reaction conditions results in a dehydrohalogenation reaction.
101. (Previously Presented) The process of claim 100, wherein the further reaction conditions includes the presence of an acid acceptor.
102. (Original) The process of claim 86, wherein the second compound is an unsaturated molecule which is not free radically (co)polymerizable and terminates the polymer.
103. (Original) The process of claim 102, wherein the unsaturated molecule comprises a second functional group.
104. (Original) The process of claim 103, further comprising:

adding a third compound comprising a third functional group, the third compound which reacts with the first functional group incorporated on the polymer.

105. (Original) The process of claim 102, wherein the unsaturated molecule is at least one of α,α -disubstituted olefin or an allyl.
106. (Original) The process of claim 94, wherein the second desired functional group comprises one of an allyl, epoxy, hydroxy, amino, cyano, carboxy, masked carboxy, alkyl, perhaloalkyl, silyl, silicon containing moiety or phosphorous containing moiety.
107. (Original) A process for a catalytic atom transfer functionalization of oligo/polymeric materials having one or more radically transferable atom(s) or group(s), comprising the steps:
 - providing a polymer having a radically transferable atom or group; and
 - adding a compound containing a α,α -disubstituted olefin group to the polymer in the presence of a transition metal complex capable of undergoing a redox reaction with the radically transferable atom or group, resulting in the addition of the compound containing the α,α -disubstituted olefin group at the site of the radically transferable atom or group and an elimination reaction involving the radically transferable atom or group to form a reactive unsaturated group.
108. (Original) The process of claim 107, wherein the substituents on the α,α -disubstituted olefin group are individually selected.
109. (Original) The process of claim 108, further comprising:
 - forming a functional polymer having a reactive exo-double bond and wherein one of the substituents is a methyl group.
110. (Original) The process of claim 109, further comprising:
 - forming a functional polymer having an endo-double bond.
111. (Original) The process of claim 110, wherein the coupling compound comprises an α -aryl styrene.
112. (Original) The process of claim 111, wherein the α -aryl styrene is selected from diphenylethylene, 1,3-bis(1-phenylethenyl)benzene, or 2,2- bis{4-(1-phenylethenyl)phenyl}propane.

113. (Original) The process of claim 107, wherein the polymeric material is an oligomer.
114. (Previously presented) The process of claim 107, wherein one substituent on the α,α -disubstituted olefin is a methyl group and the formed double bond is predominately a exo-double bond.
115. (Original) The process of claim 114, wherein a macromonomer with a reactive exo-double bond is prepared.
116. (Original) The process of claim 107, wherein the elimination reaction is enhanced by the addition of an acid acceptor.
117. (Original) The process of claim 116, wherein the acid acceptor is selected from the group consisting of basic organic molecules, linear and heterocyclic N containing compounds, ion exchange resins or inorganic acid acceptors.
118. (Original) A process for a catalytic atom transfer coupling of polymers comprising:
providing a first polymer having a first radically transferable atom or group;
adding a coupling compound containing one or more α,α -disubstituted olefin group(s) to the first polymer in the presence of a transition metal complex capable of undergoing a redox reaction with the first radically transferable atom or group, resulting in the addition of the coupling compound containing the α,α -disubstituted olefin group at the site of the first radically transferable atom or group and an elimination reaction comprising the radically transferable atom or group to form a reactive double bond; and
allowing a second polymer having a second radically transferable atom or group in the presence of the transition metal complex to add to the reactive double bond.
119. (Original) The process of claim 118, wherein the first polymer and the second polymer are substantially similar.
120. (Original) The process of claim 119, further comprising:
forming a functional polymer having an endo-bond and wherein the coupling compound comprises an α -alkyl styrene.
121. (Original) The process of claim 120, wherein the coupling compound comprises α -methyl styrene.
122. (Original) The process of claim 107, further comprising:

forming a functional polymer comprising an enol/ketone and wherein an α -substituent comprises a hydroxyl group.

123. (Original) The process of claim 118, wherein the coupling compound is a second polymer comprising an isopropenyl group.

124. (Original) The process of claim 123, wherein the α,α -disubstituted olefin group is a pendant functional group of the second polymer.

125. (Original) The process of claim 123, wherein the graft copolymer comprise the first copolymer grafted to the second copolymer within the graft copolymer chain.

126. (Original) The process of claim 118, wherein the first polymer is a mixture of (co)polymers.

127. (Original) The process of claim 118, wherein the second polymer has a similar composition and molecular weight to the first polymer.

128. (Original) The process of claim 118, wherein a molar ratio of the total moles of the first polymer and the second polymer to the moles of the coupling compound is controlled to form a third polymer of a configuration of at least one of linear, star, graft, and chain extended materials containing a residue of the first polymer and the second polymer.

129. (Original) The process of claim 128, wherein the first polymer includes two transferable atoms or groups and the coupling compound contains two α,α -disubstituted olefin groups allowing the formation of a network copolymer containing multiple units of the first polymer.

130. (Original) The process of claim 128, wherein the coupling compound contains one α,α -disubstituted olefin group, the first polymer and second polymer have one radically transferable atom or group and a molar ratio of the total moles of the first polymer and the second polymer to the moles of the coupling compound is essentially 1:0.5.

131. (Original) The process of claim 128, wherein the coupling compound contains two α,α -disubstituted olefin groups, the first polymer and second polymer each have one radically transferable atom or group and the molar ratio of the total moles of the first polymer and the second polymer to the moles coupling compound is essentially 1:0.25.

132. (Original) The process of claim 131, wherein the first polymer and the second polymer differ in at least one of molecular weight and composition and a star copolymer is formed.
133. (Original) The process of claim 132, wherein a hetero-arm star copolymer is formed.
134. (Original) The process of claim 131, wherein two α,α -disubstituted olefin groups differ in reactivity characteristics.
135. (Original) The process of claim 128, wherein the coupling compound is a compact molecule and contains three α,α -disubstituted olefin groups and wherein the molar ratio is controlled to form a star copolymer with up to six arms.
136. (Original) The process of claim 118, wherein the coupling compound contains two α,α -disubstituted olefin groups of different reactivities and the first polymer and second polymer each have two radically transferable atoms or groups resulting in one of an extended chain or coupled polymer with an α,α -disubstituted olefin group within the chain.
137. (Original) The process of claim 126, wherein the coupling compound contains three α,α -disubstituted olefin groups and the molar ratio of the total moles of the first polymer and the second polymer to the moles coupling compound is controlled to form a star polymer with up to six arms.
138. (Original) The process according to 128, wherein the molar ration is 1:0.167.
139. (Original) The process of claim 118, wherein the coupling compound comprises a third polymer.
140. (Withdrawn) A star copolymer, comprising segments of free radically polymerizable monomers wherein two or more arms have a different composition from the other arms.
141. (Withdrawn) A star copolymer produced by the process of claim 128, wherein the first polymer and the second polymer are different.
142. (Withdrawn) The star copolymer of claim 141, wherein the first polymer differs from the second polymer in at least one of molecular weight or composition.
143. (Withdrawn) A graft copolymer with a backbone polymer with incorporated coupling compounds and a grafted polymer produced by process of claim 118.

144. (Withdrawn) The graft copolymer of claim 143, wherein the backbone polymer is produced by an addition or condensation polymerization process.
145. (Withdrawn) The graft copolymer of claim 143, wherein the backbone polymer is a polyolefin.
146. (Withdrawn) The graft copolymer of claim 143, wherein the backbone polymer comprises blocks of at least one of polystyrene, polyethylene, polypropylene, polyisobutylene, polybutadiene or polyisoprene.
147. (Withdrawn) An α -substituted olefin, comprising an exo-double bond, suitable for use as a macromonomer, in which the α -substituent is a free radically (co)polymerized oligo/polymer with a molecular weight greater than 250 possessing a known group at the other terminus of the polymer.
148. (Withdrawn) An α,β -disubstituted olefin comprising two substituants, wherein each substituant is a free radically (co)polymerized oligo/polymer with a molecular weight greater than 250.
149. (Withdrawn) A macromonomer comprising:
 - a functional group containing a terminal exo-olefin double bond derived from free radically (co)polymerizable monomers;
 - a stereochemistry and tacticity of a material formed by a free radical polymerization process; and
 - a symmetrical single peak molecular weight distribution less than 1.5.
150. (Withdrawn) The macromonomer of claim 149, wherein the functionality is greater than 90 mole %.
151. (Currently amended) A controlled polymerization process, comprising:
 - adding a core forming compound to an active atom transfer radical polymerization process; and
 - forming a multi-arm star copolymer wherein polymers react reacting polymer chains having a radically transferable atom or group with the core forming compound to form the multi-arm star copolymer.
152. (Original) The process of claim 151, further comprising:
 - adding a plurality of initiators, wherein each initiator includes:
 - a radically transferable atom or group; and

optionally, a functional group.

153. (Original) The process of claim 152, wherein the core forming compound is a divinyl compound.
154. (Original) The process of claim 153, wherein the multi-arm star polymer includes a single well defined core.
155. (Original) The process of claim 153, wherein the multi-arm star polymer includes a core having core compound to core compound coupling.
156. (Original) The process of claim 153, wherein the multi-arm star polymer includes a network of coupled core compounds.
157. (Original) The process of claim 153, wherein the resulting multi-arm star polymer is a one of a gel or crosslinked system.
158. (Original) The process of claim 153, wherein the divinyl compound is one of a divinyl aryl compound, a di-acrylate or a di-methacrylate.
159. (Withdrawn) A telefunctional multi-arm star copolymer comprising:
 - a core comprising core unit to core unit coupling;
 - a plurality of arms synthesized from radically polymerizable monomers attached to at least one of the core units; and
 - a known level of functional groups on the termini of each polymer chain.
160. (Withdrawn) A crosslinked or gel-like telefunctional multi-arm star copolymer comprising:
 - at least two core units;
 - a plurality of arms synthesized from radically polymerizable monomers attached to at least one of a core unit and another arm forming a matrix; and
 - a known level of functional groups with in the matrix.
161. (Withdrawn) A telefunctional network copolymer produced by the process of claim 141, wherein:
 - the average number of radically transferable atoms or groups per first polymer is greater than one; and
 - the core compound is a divinyl compound.
162. (Withdrawn) A telefunctional multi-arm star copolymer wherein the arms of the copolymer are composed of different copolymers displaying differing properties.

163.-223. (Canceled)

224. (Withdrawn) A multifunctional star (co)polymer, comprising:

a core compound;

a plurality of polymer arms synthesized from free radically copolymerizable monomers having a functional end and an attached end, wherein the attached end is attached to the core compound;

a functional group attached to the functional end of the polymer arms.

225. (Withdrawn) The multifunctional star (co)polymer of claim 224, wherein in the polymer arms are of controlled molecular weights and wherein the functional groups present on the outer layer of the star (co)polymer have been added by an atom transfer addition reaction.

226. (Withdrawn) The polymer of claim 224, wherein the free radically copolymerizable monomers include (meth)acrylates and (meth)acrylic acids.

227. (Withdrawn – Previously Presented) The multifunctional star (co)polymer of claim 224, wherein the functional group is selected from hydroxy, epoxy, amino, cyano, halide and the functional group is present on the functional end of the polymer arms.

228.-269. (Canceled)

270. (Withdrawn) A homo-telechelic copolymer, comprising:

a polymer synthesized from free radically copolymerizable monomers having a first terminal end and a second terminal end;

a first functional group attached to said first terminal end;

a second functional group attached to said second terminal end, wherein the said second functional group has a different reactivity than said first functional group.

271. (Previously presented) A controlled polymerization process for the production of telefunctional multi-arm star copolymers, comprising:

polymerizing a free radically (co)polymerizable monomer in the presence of a system comprising:

a telefunctional multi-armed star initiator synthesized from free radically copolymerizable monomers, a first initiator with one radically transferable atom or group, and a divinyl compound in the presence of a transition metal complex.

272. (Original) The process of claim 271, wherein the first initiator further comprises a second functional group.

273.-286. (Canceled)

287. (Currently amended) A polymerization process, comprising:
radically polymerizing one or more radically (co)polymerizable monomers in the presence of a system comprising:
an initiator having one or more radically transferable atoms or groups;
a transition metal compound which participates in a reversible redox cycle with said initiator or a dormant polymer chain end;
a N-, O-, P- or S- containing ligand which coordinates in a σ -bond to the transition metal, any carbon-containing ligand which coordinates in a π -bond to the transition metal or any carbon-containing ligand; and
a polar solvent selected from methanol, ethanol, acetone, and mixtures thereof in a concentration of 5 wt% to 10 wt% of the system to form a (co)polymer.

288. (Canceled)